

MANGANESE MODIFIED NANOSCALE COBALT CATALYST TO SYNTHESIZE LONG-CHAIN HYDROCARBONS

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ABSTRACT: Cobalt catalyst supported on ZrO_2 coated SiO_2 aerogel exhibits high FTS activity and C^{5+} selectivity at a moderate pressure in fixed bed reactor. It yields 150g liquid hydrocarbons and FT wax for every cubic meter of syngas. The effect of manganese modification on structure, texture, reduction, H_2 adsorption and FTS performance of Co/ZrO_2-SiO_2 catalyst was examined. The results show that addition of proper amount of manganese lowers the methane selectivity and raises C^{5+} selectivity, but excessive amount of manganese added leads to opposite results. Carbon number distribution of $Co-Mn/ZrO_2-SiO_2$ no longer follows SF distribution. Distinct two peaks (maximum point at C_{11} and C_{17} respectively) are observed in the profile of carbon number distribution for $Co-Mn/ZrO_2-SiO_2$ indicating the existence of two kinds of active sites.

Keywords: Fischer-Tropsch Synthesis, Nanoscale Catalyst, Manganese Promoter

INTRODUCTION

Fischer-Tropsch synthesis is catalytic reaction of CO hydrogenation for obtaining C^{2+} hydrocarbons. Carbon number distribution of traditional FTS product obey Schulz-Flory distribution which constrains selectivity improvement of toward any product with particular carbon number. Research work of FTS has been concentrated on method and principle to control chain length distribution in last twenty years. Currently, the objective of most FTS research work is to increase the α value to as high as possible (0.95 or above) in order to synthesize long chain hydrocarbons (1). Different conclusions were drawn on the point of whether FTS reaction is structure sensitive (2-3). General result is that specific activity of FTS is affected by properties of support material and active metal crystal size of catalyst. Generally, the enlargement of active metal crystal size will increase the selectivity of long-chain hydrocarbons. It is because that in the process of FTS reaction, growing carbon chain lies on the surface of active metal crystals. So large metal crystal is required to obtain long-chain hydrocarbons. But for catalysts with some extent of metal-support interaction, such as Fe/AC (4) and Co/ZrO_2 (5), opposite results were obtained. Selectivity of long-chain hydrocarbons increases with the decreasing of metal crystal size. To this kind of catalyst, minimization of particle size leads to stronger metal-support interaction. Then metal support synergism plays more important role to affect FTS activity and selectivity than metal crystal size of catalyst does. Consequently, preparation of modified ultrafine FTS catalyst with metal support interaction is a promising path to synthesize long chain hydrocarbons with high activity and selectivity.

Sol-gel method is a traditional way to produce ultrafine oxides. Previously, ultrafine SiO_2 aerogel powder was prepared by sol-gel method followed by supercritical fluid drying technique. The SiO_2 aerogel powder obtained was then coated with ZrO_2 to form ZrO_2-SiO_2 complex oxide. Cobalt catalyst supported on this complex oxide is in the category of nano material, its particle size is about 9.0nm. Under moderate pressure and in a fixed bed reactor, this catalyst was proved to be an extremely suitable catalyst for synthesis of long chain hydrocarbons, C^{5+} yield could reach 150g per cubic meter of syngas (6).

Promotion effect of manganese on iron F-T catalyst was studied extensively. The promotion effect was attributed to alkali and structure promotion. One of the characteristics of alkali promotion is to improve the selectivity of long chain hydrocarbons. Consequently, promotion effect of manganese to ultrafine Co/ZrO_2-SiO_2 catalyst on the properties of

structure, texture, reduction and F-T synthesis is investigated in this paper.

EXPERIMENTAL

Catalyst preparation

Ultrafine silica aerogel was prepared by sol-gel method using TEOS as the precursor followed by supercritical fluid drying of the gels in an autoclave. The obtained monoliths were calcinated at 623K for 8hr and crushed. Zirconia coated ultrafine silica support was prepared by coating the ultrafine silica aerogel powder with solution of zirconium nitrate in a rotary evaporator. Dried sample was then calcinated at 673K in air. Preparation of cobalt catalysts was completed using incipient wetness technique with cobalt nitrate as impregnation solutions. Manganese promoted catalysts were prepared using a mixed solution of cobalt nitrate and manganese acetate as the impregnation solutions. Catalysts so obtained were then dried and calcinated before being pellesized and sieved.

Characterization

Cobalt loading of these catalysts were examined by ICP. BET surface areas and the distribution of pore volumes were measured by Micromeritics ASAP 2000 physical adsorption unit. XRD analysis were performed on a Rigaku diffractometer. X-ray photoelectron spectra were recorded with a Perkin-Elmer PHI 1600 ESCA system equipped with Al K α X-ray excitation source and hemispherical electro analyzer. TPR tests were performed in a U-shape reaction tube with a catalyst loading of 0.2g, Ar purge temperature of 473K, temperature raising rate of 10 K/min, the carrier gas was H₂/Ar (H₂ 8.6V%) and the detector was TCD. TPD tests were processed after adsorption of H₂ over catalysts reduced at 673K and cooled in ambient temperature.

Reaction tests

The catalyst precursors (5g) were loaded into fixed bed laboratory reactors and reduced in situ at 673K under hydrogen. Synthesis gas (CO/H₂=1:2) was subsequently fed over the catalysts and the system was kept at steady state before mass balance data were collected. Liquid and solid condensates were collected in two separate condensers. Product analysis for gas, liquid and solid products were all performed by GC using various columns.

RESULTS AND DISCUSSION

Texture property of Co-Mn/ZrO₂-SiO₂ catalysts

Table 1 illustrates the effect of Mn loading on texture property of Co-Mn/ZrO₂-SiO₂ catalysts. The results indicate that comparing with Co/ZrO₂-SiO₂ catalyst, the addition of manganese decreases the surface area and pore volume of Co-Mn/ZrO₂-SiO₂ catalyst and the change of average pore diameter is slight. The surface area and pore volume of three Co-Mn/ZrO₂-SiO₂ catalysts decrease with an increase of manganese loading.

Structure of Co-Mn/ZrO₂-SiO₂ catalyst

XRD spectras of Co(10.71%)-Mn(1.57%)/ZrO₂-SiO₂ catalyst before and after reaction were both recorded. We concluded that the addition of manganese increases the metal dispersion of cobalt and makes the crystal size of cobalt smaller. Furthermore, Co₂Mn₂O_{4.5} spinel phase was formed after calcination of Co(10.71%)-Mn(1.57%)/ZrO₂-SiO₂ catalyst.

Surface characterization of Co-Mn/ZrO₂-SiO₂ catalysts

Surface property of Co/ZrO₂-SiO₂ and three Co-Mn/ZrO₂-SiO₂ catalysts were studied by XPS. Binding Energy and atomic ratio of the catalysts are listed in Table 2. From comparison of results of surface and bulk atomic ratio, it is evident that beneficiation of manganese at catalysts surface is significant. On the other hand, both Co2p_{3/2} and Mn2p_{3/2} have two BE values which verifies the formation of Co,Mn spinel phase.

TPR results of Co-Mn/ZrO₂-SiO₂ catalysts

Reduction property of Co-Mn/ZrO₂-SiO₂ catalyst was investigated by TPR. The results indicated that manganese promoter reacts with a part of CoO to form Co,Mn solid solution. Therefore the

reduction of CoO is hindered and the reduction degree of catalysts in 673K decreases with the increasing manganese loading.

FTS performance of Co-Mn/ZrO₂-SiO₂ catalysts

The component of a catalyst affects the FTS performance significantly. The change of FTS performance at the same reaction temperature (493K), with the increase of manganese loading, are listed in Table 3. The following conclusions could be drawn:

- 1) CO conversion rate decreases.
- 2) Olefin to paraffin ratio increases evidently and then decreases. And olefin to paraffin ratios of all Co-Mn/ZrO₂-SiO₂ catalysts are higher than that of Co/ZrO₂-SiO₂.
- 3) CH₄ selectivity decreases to a minimum and then increases.
- 4) C⁵⁺ selectivity increases to maximum and then decrease.
- 5) Wax to oil weight ratio increases to maximum and then decreases.

The results indicate that certain amount of manganese addition could increase the selectivity of longer chain hydrocarbons, while excess amount of manganese addition leads to opposite results. FTS performance of Co-Mn/ZrO₂-SiO₂ is explained as the followings:

Decrease of CO conversion rate. (1) Addition of Mn promoter dilutes and covers the Co active sites. (2) The reduction of CoO was hindered by Mn and the degree of reduction of the catalysts at 673K decreases.

Increase of olefin to paraffin ratio. (1) Manganese as a texture promoter. Addition of Mn makes cobalt crystal size get smaller. Small crystal size makes newly produced olefins leave the surface of the catalyst quickly and increase the diffusion of olefin. Therefore, the secondary hydrogenation of olefins is restrained. (2) Group effect caused by beneficial of manganese on catalyst surface. Cobalt active sites are divided into smaller groups and this kind of surface modification restrains the hydrogenation of catalysts effectively. (3) Manganese as an electron promoter. Addition of Mn enhances the d- π feedback of Co to Co and therefore weakens Co-H bond.

Decrease of CH₄ selectivity and increase of C⁵⁺ selectivity. (1) Manganese as an alkali promoter. One of the characteristic of alkali promoter in FTS catalyst is to increase the selectivity of longer-chain hydrocarbons. (2) Group effect of manganese. The formation of methane requires a relatively large distribution of active center groups.

Fig.1 is the products carbon number distribution for Co/ZrO₂-SiO₂ and Co(10.71%)-Mn(1.57%)/ZrO₂-SiO₂ catalysts. It can be seen that carbon number distribution of Co/ZrO₂-SiO₂ catalyst follows Schulz-Flory distribution while that of Co-Mn/ZrO₂-SiO₂ catalyst deviates SF distribution and have two peaks instead. The maximum points are C₁₁ and C₁₇, respectively. Double-peaks distribution indicates the existence of two kinds of active centers. The author ascribes the active centers to be Co and Co,Mn spinel separately. The assumption were verified by the results of Hongwei Xiang on Co-Mn/ZrO₂ catalyst and Yongqing Zhang on Co-Cr/ZrO₂-SiO₂ catalyst(7).

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Table 1 Texture property of oxidation state Co-Mn/ZrO₂-SiO₂ catalysts

Catalysts	Co/Mn	S _{BET} area	V _{PN}	r _p
	Atomic ratio	(m ² /g)	(cm ³ /g)	(nm)
Co(10.73%)/ZrO ₂ -SiO ₂		421.8	0.53	5.0
Co(10.71%)-Mn(1.57%)/ZrO ₂ -SiO ₂	6.82	378.9	0.51	5.0
Co(11.58%)-Mn(3.28%)/ZrO ₂ -SiO ₂	3.53	359.9	0.45	5.0
Co(11.09%)-Mn(4.36%)/ZrO ₂ -SiO ₂	2.54	350.5	0.40	4.6

Table 2 Binding Energy and atomic ratio of Co-Mn/ZrO₂-SiO₂ catalysts

Catalysts	Binding Energy (eV)				Co/Mn atomic ratio	
	Co2p _{3/2} percent		Mn2p _{3/2} percent		bulk	surface
Co(10.73%)/ZrO ₂ -SiO ₂	777.91	37.87				
	780.74	62.13				
Co(11.58%)-Mn(3.28%)/ZrO ₂ -SiO ₂	777.95	41.68	641.58	81.88	3.53	2.30
	780.57	58.32	645.40	18.12		
Co(10.71%)-Mn(1.57%)/ZrO ₂ -SiO ₂	779.05	72.75	641.09	86.78	6.82	4.17
	781.46	27.25	644.93	13.22		

Table 3. FTS performance of catalysts

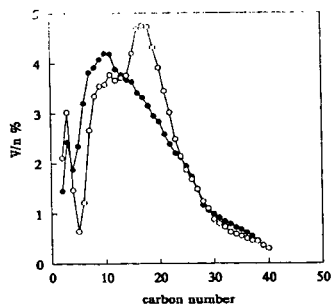
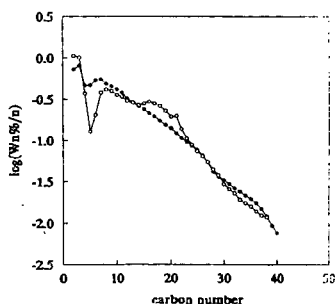
Catal. No.	CO conv. (%)	HC distri. (wt%)		O/P ^a ratio	Yield[g/Nm ³ (CO+H ₂)]		Wax/Oil (wt)
		C ₁	C ⁵⁺		C ¹⁺	C ⁵⁺	
1	96.38	13.66	81.09	0.092	186.60	151.30	0.81
2	92.31	9.08	87.16	0.15	177.69	154.89	0.91
3	89.80	13.66	79.14	0.41	184.58	146.08	1.57
4	82.81	27.52	57.40	0.21	113.97	65.51	0.21

Reaction conditions: H₂/CO=2, P=2.0MPa, T=473K, GHSV=500h⁻¹

a: olefin to paraffin ratio.

No.1: Co(10.73%)/ZrO₂-SiO₂ No.2: Co(10.71%)-Mn(1.57%)/ZrO₂-SiO₂

No.3: Co(11.58%)-Mn(3.28%)/ZrO₂-SiO₂ No.4: Co(11.09%)-Mn(4.36%)/ZrO₂-SiO₂

Fig 1. Carbon number distribution of products over (a): Co/ZrO₂-SiO₂ and (b): Co-Mn/ZrO₂-SiO₂Fig 2. Schulz-Flory distribution of products over (a): Co/ZrO₂-SiO₂ and (b): Co-Mn/ZrO₂-SiO₂